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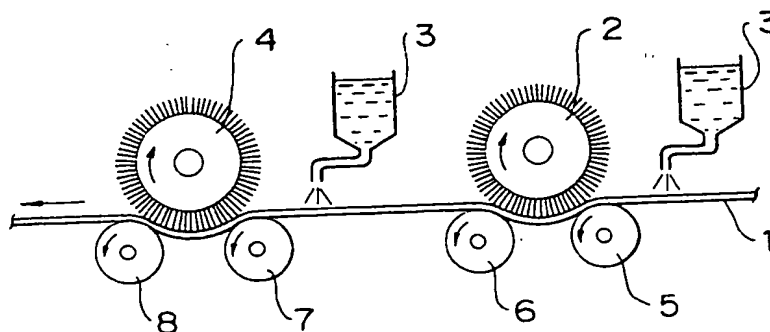
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(54) Method for preparing an aluminum substrate for lithographic printing plate.

(57) A method of preparing an aluminum substrate for lithographic printing plate comprises a brush-graining step which comprises surface-roughening an aluminum plate with at least two kinds of brushes whose bristles have different diameters. The lithographic printing plate prepared using the aluminum substrate brush-grained by the foregoing method hardly causes, on a printing press, background contamination and narrowing and/or collapse of the shadowed portion thereof. Therefore, the printing plate can easily be handled even by an inexperienced person and can stably provide high quality copies as compared with conventional printing plates.

**FIG. 1****EP 0 595 179 A1**

## BACKGROUND OF THE INVENTION

The present invention relates to a method for preparing an aluminum substrate for lithographic printing plate and more specifically to a method for preparing an aluminum substrate for lithographic printing plate which comprises specifically designed brush-graining processes.

The lithographic printing method is a printing method which makes use of the fact that water is not substantially miscible with oils. Thus, there are formed, on the plate surface of a lithographic printing plate used in this printing method, a region which receives water and repels an oil-based ink (hereunder referred to as "non-image portion") and a region which repels water and receives an oil-based ink (hereunder referred to as "image portion").

The aluminum substrate is used, in the lithographic printing plate, for carrying non-image portions on the surface thereof and; therefore, must satisfy various requirements of properties which are in conflict with one another, such as excellent hydrophilicity and water retention characteristics as well as excellent adhesion to a light-sensitive layer subsequently applied thereto. If the substrate has low hydrophilicity, an ink is adhered to non-image portions of the resulting lithographic printing plate during printing operations and this results in the so-called background contamination. On the other hand, the use of a substrate having poor water retention characteristics leads to the phenomenon of ink-spreading in shadowed portions unless a large amount of dampening water is used. Thus, so-called water tolerance of the resulting lithographic printing plate becomes narrow.

To prepare an aluminum substrate excellent in these properties, fine irregularities are in general formed on the surface of an aluminum plate by a surface-graining treatment. As such surface-graining treatments, these have been known, for instance, mechanical surface-graining methods such as ball-graining, brush-graining, wire-graining and blast-graining; electrolytic surface-graining methods such as a method comprising electrolytically etching an aluminum plate in an electrolyte containing hydrochloric acid and/or nitric acid; and combined surface-roughening methods comprising combinations of mechanical surface-roughening treatments and electrolytic surface-roughening treatments as disclosed in U.S. Patent No. 4,476,006.

Among these surface-graining methods, effectively used are, for instance, a method for surface-graining through brush-graining and a surface-graining method comprising a combination of brush-graining and electrolytic surface-roughening since they can provide substrates for lithographic printing plate excellent in quality and they are adapted for mass-production. In the brush-graining process, however, there have generally been used a brush whose bristles are prepared from one kind of specific material and have one kind of specific bristle-size (diameter of bristle) and cross-sectional shape even when a plurality of brushes are used.

However, aluminum substrates surface-grained by a brush-graining method which makes use of only one kind of brush or by a multi-graining method comprising a combination of brush-graining and electrolytic surface-roughening treatments have still been insufficient in hydrophilicity, water retention characteristics and adhesion to a light-sensitive layer subsequently applied thereto. In other words, the irregularities of the roughened surface should be shallow and smooth to some extent to improve the hydrophilicity thereof to a preferred level, but this results in a decrease in the amount of water retained and impairs the adhesion to a light-sensitive layer subsequently applied, while if deeper irregularities are formed on the aluminum substrate, the water retention characteristics thereof is increased, or the water tolerance becomes wider and the adhesion to a light-sensitive layer is improved, but this results in background contamination during printing operations.

Recently, speeding up and automation of plate-making processes and printing operations have increasingly been forwarded and there has not been enough of trained labor, in the field of lithographic printing. Under such present circumstances, there has been desired for the development of a stable lithographic printing plate which allows easy printing operations even by unskilled persons and which has quality higher than that accomplished by the conventional lithographic printing plate, i.e., a lithographic printing plate which has wide water tolerance and is hardly contaminated.

## SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to provide a substrate for presensitized plate for use in making a lithographic printing plate (hereinafter referred to as "PS plate") which has high water retention characteristics and accordingly, does not cause any collapse of shadowed portions even when the amount of dampening water is reduced, which is hardly contaminated and which is excellent in the adhesion to a light-sensitive layer subsequently applied thereto.

The inventors of this invention have conducted various studies to achieve the foregoing object, have found out that the foregoing object can effectively be accomplished by a novel mechanical surface-roughening method in which an aluminum plate is surface-roughened through the use of at least two kinds of brushes whose bristles have different diameters and thus have completed the present invention.

According to the present invention, there is thus provided a method of preparing an aluminum substrate for lithographic printing plate comprising a brush-graining step which comprises surface-roughening an aluminum plate with at least two kinds of brushes whose bristles have different diameters.

## BRIEF EXPLANATION OF THE DRAWINGS

Fig. 1 is a schematic diagram for explaining an embodiment of the method of the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

The method of preparing an aluminum substrate for lithographic printing plate according to the present invention will be explained in detail below while referring to the attached drawing.

### Aluminum Substrate

The aluminum plate used in the invention is selected from the group consisting of pure aluminum plate, aluminum alloy plates comprising aluminum as main component and trace amounts of other elements as well as plastic films laminated with an aluminum film or on which aluminum is vapor-deposited. Examples of the trace elements included in the aluminum alloys are silicon, iron, manganese, copper, magnesium, chromium, zinc, bismuth, nickel and/or titanium. The amount of these trace elements present in the aluminum alloy is not more than 10% by weight. Preferred aluminum plate used in the invention is a pure aluminum plate, but it is presently difficult to obtain completely pure aluminum plate from the viewpoint of refining techniques. Therefore, an aluminum plate containing other elements in a trace amount may be used. As has been discussed above, the aluminum plates usable in the invention are not restricted to those having specific compositions, may be those commonly known and used in this art and thus may appropriately be selected from, for instance, JIS A 1050, JIS A 1100, JIS A 3103 and JIS A 3005. The aluminum plate used in the invention has a thickness in the order of about 0.1 to 0.6 mm.

The aluminum plate is, if desired, degreased by treating with, for instance, a surfactant solution, an organic solvent or an alkaline aqueous solution for the removal of the rolling oils present on the surface thereof prior to the brush-graining treatment, but the degreasing treatment may be omitted. Subsequently, the aluminum plate is subjected to the brush-graining using at least two kinds of brushes having different bristle-diameters while supplying a slurry of an abrasive to the surface of the plate.

In the brush-graining, a brush initially used in the process is called a first brush and a brush used in the final brush-graining process is called a second brush. In the brush-graining process, an aluminum plate 1 is sandwiched between a roll-like brush (2 or 4) and two support rolls (5 and 6; or 7 and 8) as will be seen from Fig. 1. In each set of the roll-like brush (2 or 4) and two support rolls (5 and 6; or 7 and 8) these two support rolls in each set are arranged in such a manner that the shortest distance between the outer surfaces of the support rolls is smaller than the outer diameter of each corresponding roll-like brush. It is thus preferred to carry out the graining of the surface of the aluminum plate 1 by conveying it at a constant velocity and pressing it against the roll-like brush 2 or 4 so that it is forced into the space between the support rolls 5 and 6 or 7 and 8, while supplying a slurry 3 of an abrasive onto the surface of the aluminum plate and rotating the roll-like brush to perform surface-graining.

The brush preferably used in the invention may be those each comprising a roll-like base and bristles of a brush material such as nylon, polypropylene, animal hairs or steel wire having a uniform length which are implanted in and uniformly distributed on the base; those each comprising a base having small holes and bundles of bristles implanted in the holes of the base; or channel roll type ones. Among the foregoing brushes, particularly preferred are those comprising nylon bristles having a bristle length preferably ranging from 10 to 200 mm as determined after the implantation. The diameter of the roll-like base preferably ranges from 20 to 60 cm, and more preferably from 30 to 50 cm.

The density of bristles to be implanted in a brush roll preferably ranges from 30 to 1000 bristles/cm<sup>2</sup> and more preferably 50 to 300 bristles/cm<sup>2</sup>. The preferred diameter of the bristles is not less than 0.57 mm and not more than 1.20 mm, more preferably not less than 0.64 mm and not more than 1.00 mm for the first brush; and not less than 0.10 mm and not more than 0.34 mm, more preferably not less than 0.20 mm and not more than 0.30 mm for the second brush.

If the diameter of the bristles for the first brush is less than 0.57 mm, the resulting aluminum substrate does not ensure water retention characteristics sufficient for preventing any collapse of shadowed portions when the amount of dampening water is reduced during printing operations.

The second brush comprising fine bristles having a diameter of not more than 0.34 mm is used for smoothening the sharp convexes on the grained surface formed through the graining by the first brush comprising thick bristles having a diameter of not less than 0.57 mm and for preventing the occurrence of background contamination during printing. For this reason, if the bristles of the second brush have a diameter of greater than 0.34 mm, a desired effect of sufficiently preventing background contamination cannot be ensured.

The number of the first brush used in the invention is not restricted to a specific number, but preferably 1 to 10 and more preferably 1 to 6 brushes.

On the other hand, the number of the second brushes to be used in the invention is not likewise be limited to a specific number, but preferably 1 to 3 and more preferably 1 to 2 brushes.

In an integrated system for producing substrates in which each process for treating the substrates is continuously carried out, it is necessary to reduce the time required for each process as short as possible. In this respect, it is desirable to increase the number of brushes used, in particular the number of the first brushes as the time required for the brush-graining is reduced.

The rotational number of the brush roll can arbitrarily be selected so that it falls within the range of from 200 rpm to 2000 rpm. The support rolls used have rubbery or metallic surfaces and excellent straightness.

The brush rolls are preferably rotated in the direction along the conveying direction of the aluminum plate as shown in Fig. 1, but some of the brush rolls may be rotated in the direction opposite to the conveying direction of the aluminum plate if a plurality of brush rolls are used.

A substrate having all of the desired properties such as hydrophilicity, water retention characteristics and adhesion to a light-sensitive layer subsequently applied thereto to form a light-sensitive material such as a PS plate can be obtained by first surface-roughening the plate with the foregoing brush having thick bristles and then treating it with a brush having fine bristles according to the present invention.

Thus, the present invention can ensure various effects. For instance, the aluminum substrate prepared by the invention shows wide water tolerance and can provide a lithographic printing plate which hardly causes background contamination since the plate does not cause any collapse of shadowed portions when the amount of dampening water used is reduced. Moreover, the plate never suffers from any deterioration of the adhesion to the subsequently applied light-sensitive layer. In addition, the present invention ensures a dot gain-reducing effect during printing operations, although the mechanism thereof has not yet been clearly elucidated.

The slurry of an abrasive herein used preferably comprises an abrasive having a particle size ranging from 15 to 35  $\mu\text{m}$  such as quartz sand, alumina powder, volcanic ash, carborundum and emery dispersed in water in a concentration preferably ranging from 10 to 70% by weight.

The substrate is preferably treated in such a manner that the center line average roughness ( $R_a$ : surface roughness) of the substrate prepared by the method of the invention falls within the range of from 0.5 to 1.0  $\mu\text{m}$  (the tracer 10  $\mu\text{mR}$ ).

After brush-graining the aluminum plate in the foregoing manner, it is preferred to chemically etch the surface of the plate. The chemical etching serves to remove the abrasive particles and aluminum scraps cutting into the surface of the brush-grained aluminum plate. After the etching, the aluminum plate is electrochemically surface-roughened and, as a result, these treatments ensures the formation of a uniformly and effectively surface-roughened aluminum plate.

Such chemical etching methods are detailed in U.S. Patent No. 3,834,998. More specifically, the method comprises immersing an aluminum plate in a solution capable of dissolving aluminum, such as an aqueous solution of an acid or a base. Examples of the acids usable in this etching treatment are sulfuric acid, persulfuric acid, hydrofluoric acid, phosphoric acid, nitric acid and hydrochloric acid, while examples of the bases include sodium hydroxide, potassium hydroxide, sodium tertiary phosphate, potassium tertiary phosphate, sodium aluminate, sodium metasilicate and sodium carbonate. Among these, preferred are aqueous solutions of bases because of high etching rates. The chemical etching treatment is generally carried out in an aqueous solution having an acid or alkali concentration ranging from 0.05 to 40% by weight at an etching temperature ranging from 40 to 100 °C for 5 to 300 seconds.

When the chemical etching is performed in an aqueous solution of a base, smut is usually formed on the surface of the aluminum plate. In such case, the aluminum plate is preferably subjected to the so-called desmutting treatment in which the plate is treated with phosphoric acid, nitric acid, sulfuric acid, chromic acid or a mixture thereof.

Subsequently, the aluminum plate is, if desired, electrochemically surface-roughened. The electrochemical surface-roughening treatment may comprise, for instance, passing an alternating or direct current through the plate in an electrolyte such as a hydrochloric acid or nitric acid solution. It is also possible to use a method comprising a combination of DC and AC electrochemical surface-roughening treatments as disclosed in Japanese Un-examined Patent Publication (hereunder referred to as "J.P. KOKAI") No. Sho 54-63902 (= U.S. Patent No. 4,476,006).

The concentration of hydrochloric acid or nitric acid in an electrolyte used preferably ranges from 0.01 to 3% by weight and more preferably 0.05 to 2.5% by weight.

Moreover, the electrolyte may further comprise anticorrosive agents (or stabilizers) and/or grain-uniformizing agents such as nitrates, chlorides, monoamines, diamines, aldehydes, phosphoric acid, chromic acid, boric acid and aluminum oxalate. Further the electrolyte may comprise a proper amount (1 to 10 g/l) of aluminum ions.

The electrochemical surface-roughening treatment is in general performed at an electrolyte temperature ranging from 10 to 60 °C. The alternating current used in this treatment may be those having rectangular waveform, trapezoidal wave form or sinusoidal wave form so far as the polarity thereof is alternatively exchanged. Thus, the alternating current may be single phase and three phase alternating currents which are usually used as commercial alternating currents. Moreover, the electrochemical surface-roughening treatment is desirably carried out at a current density ranging from 5 to 100 A/dm<sup>2</sup> for 10 to 300 seconds.

Preferably, the aluminum plate thus surface-roughened is, if desired, desmuted by treating with a 10 to 50% hot sulfuric acid solution (40 to 60 °C) or a dilute alkali solution (such as an aqueous solution of sodium hydroxide). If the desmutting treatment is carried out with an alkali solution, the plate is subsequently immersed in an acid solution (such as nitric acid or sulfuric acid) for washing and neutralizing the plate.

The aluminum plate thus processed is, if desired, anodized for the improvement in the water retention characteristics and wear resistance of the surface. Electrolytes used in the anodization of the aluminum plate is not restricted to specific ones so far as they can form porous anodized layers and in general may be, for instance, sulfuric acid, phosphoric acid, oxalic acid, chromic acid or mixture thereof. The concentrations of these electrolyte can appropriately be determined depending on the kinds thereof.

The conditions for the anodization vary depending on the kinds of electrolytes selected and, therefore, cannot unconditionally be determined, but in general the anodization is suitably carried out at an electrolyte concentration ranging from 1 to 80% by weight, an anodization temperature ranging from 5 to 70 °C, a current density ranging from 1 to 60 A/dm<sup>2</sup>, an electric voltage ranging from 1 to 100 V for an electrolyzation time ranging from 10 seconds to 5 minutes.

In the anodization carried out in a sulfuric acid solution as an electrolyte, the aluminum plate is usually treated by a direct current, but an alternating current may likewise be used in this anodization method. This electrolyzation treatment is performed at a sulfuric acid concentration ranging from 5 to 30% and a temperature ranging from 20 to 60 °C for 5 to 250 seconds. The electrolyte preferably comprises aluminum ions. The current density used in this treatment preferably ranges from 1 to 20 A/dm<sup>2</sup>.

In the anodization carried out in a phosphoric acid solution as an electrolyte, the aluminum plate is treated at a phosphoric acid concentration ranging from 5 to 50%, a temperature ranging from 30 to 60 °C, a current density ranging from 1 to 15 A/dm<sup>2</sup> for an anodization time ranging from 10 to 300 seconds.

The amount of the anodized layer thus formed is preferably not less than 1.0 g/m<sup>2</sup> and more preferably 2.0 to 6.0 g/m<sup>2</sup>. This is because if it is less than 1.0 g/m<sup>2</sup>, the resulting aluminum substrate provides a lithographic printing plate having insufficient printing durability, the non-image portions of the lithographic printing plate are easily damaged and this often leads to so-called "contamination due to defects", i.e., adhesion of an ink to these defects during printing operations.

After the anodization treatment, the surface of the aluminum plate is, if necessary, subjected to a hydrophilization treatment. The hydrophilization used in the invention may be treatments with alkali metal silicates (such as aqueous sodium silicate solution) as disclosed in U.S. Patent Nos. 2,714,066, 3,181,461, 3,280,734 and 3,902,734. According to these methods, the aluminum substrate is treated by immersing or electrolyzing in an aqueous sodium silicate solution.

In addition to the foregoing methods, the aluminum substrate may likewise be hydrophilized by treating with potassium fluorozirconate as disclosed in Japanese Patent Publication for Opposition Purpose (hereunder referred to as "J.P. KOKOKU") No. Sho 36-22063 (= U.S. Patent No. 2,946,683) and by treating with polyvinyl phosphonic acid as disclosed in U.S. Patent Nos. 3,276,868, 4,153,461 and 4,689,272.

Preferred aluminum substrates further include those subjected to a sealing treatment after surface-graining and anodization treatments. The sealing treatment comprises immersing the aluminum plate in hot water or a hot aqueous solution containing an inorganic salt or organic salt or exposing the plate to water

vapor.

## PS Plate

### 5 Under-Lying Layer

An organic underlying layer is also applied, if desired, onto the aluminum plate prior to the application of a light-sensitive layer. Organic compounds used in the organic underlying layer are, for instance, carboxymethyl cellulose, dextrin, gum arabic, phosphonic acids carrying amino groups such as 2-aminoethyl phosphonic acid, organic phosphonic acids which may have substituents such as phenylphosphonic acid, naphthylphosphonic acid, alkylphosphonic acid, glycerophosphonic acid, methylenediphosphonic acid and ethylenediphosphonic acid, organic phosphoric acids which may have substituents such as phenylphosphoric acid, naphthylphosphoric acid, alkylphosphoric acid and glycerophosphoric acid, organic phosphinic acids which may have substituents such as phenylphosphinic acid, naphthylphosphinic acid, alkylphosphinic acid and glycerophosphinic acid, amino acids such as glycine and  $\beta$ -alanine, hydrochlorides of amines having hydroxyl groups such as triethanolamine hydrochloride. These compounds may be used alone or in combination.

The organic layer can be formed by a method comprising the steps of applying a solution of the foregoing organic compound dissolved in a solvent selected from water, an organic solvent such as methanol, ethanol, methyl ethyl ketone or a mixture thereof to the hydrophilized aluminum plate and then drying or a method comprising the steps of dipping the hydrophilized aluminum plate in a solution of the foregoing organic compound dissolved in a solvent selected from water, an organic solvent such as methanol, ethanol, methyl ethyl ketone or a mixture thereof to adsorb the compound on the plate, then washing with, for instance, water and drying. In the former method, a coating solution containing the organic compound in a concentration ranging from 0.005 to 10% by weight can be applied by a variety of methods such as coating with a bar coater, a whirler and a spray device or curtain coating, while in the latter method, the concentration of the solution ranges from 0.01 to 20% by weight, preferably 0.05 to 5% by weight and the dipping temperature ranges from 20 to 90 °C, preferably 25 to 50 °C and the dipping time ranges from 0.1 second to 20 minutes, preferably 2 seconds to one minute.

The pH value of the solutions herein used may be adjusted to 1 to 12 with a basic substance such as ammonia, triethylamine or potassium hydroxide, or an acidic substance such as hydrochloric acid or phosphoric acid. Moreover, a yellow dye can be added for the improvement of tone reproduction of the resulting PS plates.

The coated amount (weighed after drying) of the organic underlying layer suitably ranges from 2 to 200 mg/m<sup>2</sup>, preferably 5 to 100 mg/m<sup>2</sup>. This is because, if the coated amount is less than 2 mg/m<sup>2</sup>, the printing durability of the resulting lithographic printing plate is insufficient, while if it exceeds 200 mg/m<sup>2</sup>, sufficient printing durability cannot likewise be obtained.

### Back Coat Layer

A coating layer of an organic polymer (hereinafter referred to as "back coat layer") may be applied onto the back face of the PS plate which makes use of the substrate prepared according to the present invention to prevent the formation of defects observed when the PS plates are put in stack.

The principal component for the back coat layer is at least one member selected from the group consisting of saturated copolymerized polyester resins, phenoxy resins, polyvinyl acetal resins and copolymerized vinylidene chloride resins, having glass transition points of not less than 20 °C.

The saturated copolymerized polyester resin comprises repeating units derived from a dicarboxylic acid and a diol. The dicarboxylic acid units of the polyesters used in the invention are, for instance, those derived from aromatic dicarboxylic acids such as phthalic acid, terephthalic acid, isophthalic acid, tetrabromophthalic acid and tetrachlorophthalic acid; and saturated aliphatic dicarboxylic acids such as adipic acid, azelaic acid, succinic acid, oxalic acid, suberic acid, sebacic acid, malonic acid and 1,4-cyclohexanedicarboxylic acid.

In addition to the foregoing component, the back coat layers may, if desired, comprise dyes and/or pigments for coloring the layer; agents for improving the adhesion to an aluminum substrate such as silane coupling agents, diazo resins comprising diazonium salts, organic phosphonic acids, organic phosphoric acids and cationic polymers; and agents usually used as lubricating agents such as waxes, higher fatty acids, higher fatty acid amides, silicone compounds derived from dimethylsiloxane, modified dimethylsiloxanes and polyethylene powder.

The thickness of the back coat layer is basically selected such that a light-sensitive layer subsequently applied thereto is not damaged even if any interleaf is not used and preferably ranges from 0.01 to 8  $\mu\text{m}$ . If it is less than 0.01  $\mu\text{m}$ , the formation of scratch marks cannot be prevented when the resulting PS plates are handled while putting them in stack. On the other hand, if the thickness thereof exceeds 8  $\mu\text{m}$ , the back coat layer gets swollen through the action of agents used in the environment surrounding the resulting printing plate during printing operation and thus suffers from change in the thickness thereof. This sometimes leads to change in the printing pressure depending on the position and hence deterioration of printing properties of the plate.

The back coat layer may be applied onto the back face of an aluminum substrate by a variety of methods. For instance, the back coat layer may be prepared by a method comprising applying, onto the aluminum substrate, the foregoing components for the back coat layer in the form of a solution or an emulsion dissolved or dispersed in a proper solvent and then drying; a method comprising forming the foregoing components into a film and adhering the film, to the aluminum substrate, through the use of an adhesive or application of heat; and a method comprising extruding the components into a molten film through a melt extruder and then adhering the molten film to the substrate with the method comprising applying the components in the form of a solution and then drying being most preferred since it can ensure the coated amount (thickness) defined above. Examples of solvents used in this method are organic solvents disclosed in J.P. KOKAI No. Sho 62-251739 (= U.S. Patent No. 4,764,450) which may be used alone or in combination.

#### Light-Sensitive Layer

A light-sensitive layer of a known light-sensitive composition is applied onto the aluminum plate which is prepared by the method detailed above and has a hydrophilized surface to give a PS plate. Examples of light-sensitive compositions usable herein include positive-working light-sensitive compositions mainly comprising o-quinonediazide compounds; and negative-working light-sensitive compositions mainly comprising photopolymerizable compounds which mainly comprise diazonium salts, alkali-soluble diazonium salts and/or unsaturated double bond-containing monomers and cinnamic acid or dimethylmaleimido group-containing photocrosslinkable compounds as light-sensitive substances.

It is also possible to use light-sensitive layers for electrophotography as disclosed in J.P. KOKOKU Nos. Sho 37-17172, Sho 38-6961, Sho 59-36259 and Sho 59-25217 and J.P. KOKAI Nos. Sho 56-107246, Sho 60-254142, Sho 56-146145, Sho 62-194257, Sho 57-147656, Sho 58-100862 and Sho 57-161863.

Among the foregoing light-sensitive substances, examples of the photopolymerizable compositions mainly comprising unsaturated double bond-containing monomers are those comprising addition polymerizable unsaturated compounds each having at least two terminal ethylene groups and photopolymerization initiators as disclosed in U.S. Patent Nos. 2,760,863 and 3,060,023 and J.P. KOKAI No. Sho 59-53836.

Examples of negative-working light-sensitive compositions comprising dimethylmaleimido group-containing photocrosslinkable compounds are light-sensitive substances as disclosed in J.P. KOKAI Nos. Sho 52-988, Hei 3-288853 and Hei 4-25845 and European Patent No. 0410654.

Among these, o-naphthoquinonediazide compounds used in positive-working light-sensitive compositions are preferably esters of 1,2-diazonaphthoquinone sulfonic acid with pyrogallol • acetone resins as disclosed in J.P. KOKOKU No. Sho 43-28403. Other preferred examples of o-quinonediazide compounds are esters of 1,2-diazonaphthoquinone-5-sulfonic acid with phenol-formaldehyde resins as disclosed in U.S. Patent Nos. 3,046,120 and 3,188,210; and esters of 1,2-diazonaphthoquinone-1-sulfonic acid with phenol-formaldehyde resins as disclosed in J.P. KOKAI Nos. Hei 2-96163, Hei 2-96165 and Hei 2-96761. Other useful o-naphthoquinonediazide compounds are, for instance, those disclosed in various patents such as J.P. KOKAI Nos. Sho 47-5303, Sho 48-63802, Sho 48-63803, Sho 48-96575, Sho 49-38701 and Sho 48-13854, J.P. KOKOKU Nos. Sho 37-18015, Sho 41-11222, Sho 45-9610 and Sho 49-17481, U.S. Patent Nos. 2,797,213, 3,453,400, 3,544,323, 3,573,917, 3,674,495 and 3,785,825, U.K. Patent Nos. 1,227,602, 1,251,345, 1,267,005, 1,329,888 and 1,330,932 and German Patent No. 854,890.

Particularly preferred o-naphthoquinonediazide compounds are those obtained through the reaction of polyhydroxy compounds having molecular weight of not more than 1,000 with 1,2-diazonaphthoquinonesulfonic acid. Specific examples thereof are those disclosed in, for instance, J.P. KOKAI Nos. Sho 51-139402, Sho 58-150948, Sho 58-203434, Sho 59-165053, Sho 60-121445, Sho 60-134235, Sho 60-163043, Sho 61-118744, Sho 62-10645, Sho 62-10646, Sho 62-153950, Sho 62-178562 and Sho 64-76047; and U.S. Patent Nos. 3,102,809; 3,126,281; 3,130,047; 3,148,983; 3,184,310; 3,188,210 and 4,639,406.

These o-naphthoquinonediazide compounds are preferably obtained through reactions of polyhydroxy compounds with 1,2-diazonaphthoquinonesulfonic acid chloride in an amount ranging from 0.2 to 1.2 eq,

more preferably 0.3 to 1.0 eq per unit equivalent of hydroxyl group of the former. The 1,2-diazonaphthoquinonesulfonic acid chloride may be either 1,2-diazonaphthoquinone-5-sulfonic acid chloride or 1,2-diazonaphthoquinone-4-sulfonic acid chloride.

In this respect, the resulting o-naphthoquinonediazide compound is a mixture of products variously differing in the positions of 1,2-diazonaphthoquinonesulfonate groups and the amounts thereof introduced, but preferred are those having a rate of the compound whose hydroxyl groups are all converted into 1,2-diazonaphthoquinonesulfonic acid esters (content of the completely esterified compound) of not less than 5 mole%, more preferably 20 to 99 mole%.

The light-sensitive composition used in the invention preferably comprises the positive-working light-sensitive compounds (inclusive of the foregoing combination) in an amount ranging from 10 to 50% by weight and more preferably 15 to 40% by weight.

The positive-working light-sensitive composition may comprise only o-quinonediazide compounds such as those listed above, but preferably the o-quinonediazide compounds are used in combination with an alkaline water-soluble resin as a binder. Examples thereof are alkaline water-soluble novolak resins such as phenol-formaldehyde resins and cresol-formaldehyde resins, for instance, o-, m- and p-cresol-formaldehyde resins, m-/p- mixed cresol-formaldehyde resins and phenol-mixed cresol (m-/p-/o- or m-/p- or m-/o-) formaldehyde resins.

Other binders usable in the invention further include phenol-modified xylene resins, polyhydroxystyrenes, halogenated polyhydroxystyrenes and acrylic resins having phenolic hydroxyl groups as disclosed in J.P. KOKAI No. Sho 51-34711 (= U.S. Patent No. 5,182,183).

Examples of suitable binders may further include copolymers generally having a molecular weight of 10,000 to 200,000 and having structural units derived from the following monomers (1) to (13).

(1) (Meth)acrylamides, (meth)acrylic acid esters and hydroxystyrenes each having an aromatic hydroxy group such as N-(4-hydroxyphenyl) (meth)acrylamide; o-, m- or p-hydroxystyrene and o-, m- or p-hydroxyphenyl-(meth)acrylate.

(2) (Meth)acrylic acid esters each having an aliphatic hydroxy group such as 2-hydroxyethyl (meth)acrylate.

(3) Unsaturated carboxylic acids such as (meth)acrylic acid, maleic anhydride and mesaconic acid.

(4) (Substituted) acrylates such as methyl acrylate, ethyl acrylate, propyl acrylate, butyl acrylate, amyl acrylate, hexyl acrylate, cyclohexyl acrylate, octyl acrylate, phenyl acrylate, benzyl acrylate, 2-chloroethyl acrylate, 4-hydroxybutyl acrylate, glycidyl acrylate and N-dimethylaminoethyl acrylate.

(5) (Substituted) methacrylates such as methyl methacrylate, ethyl methacrylate, propyl methacrylate, butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, octyl methacrylate, phenyl methacrylate, benzyl methacrylate, 2-chloroethyl methacrylate, 4-hydroxybutyl methacrylate, glycidyl methacrylate and N-dimethylaminoethyl methacrylate.

(6) (Meth)acrylamides such as (meth)acrylamide, N-methylol (meth)acrylamide, N-ethyl (meth)acrylamide, N-hexyl (meth)acrylamide, N-cyclohexyl (meth)acrylamide, N-hydroxyethyl (meth)acrylamide, N-phenyl (meth)acrylamide, N-benzyl (meth)acrylamide, N-nitrophenyl (meth)acrylamide and N-ethyl-N-phenyl (meth)acrylamide.

(7) Vinyl ethers such as ethyl vinyl ether, 2-chloroethyl vinyl ether, hydroxyethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, octyl vinyl ether and phenyl vinyl ether.

(8) Vinyl esters such as vinyl acetate, vinyl chloroacetate, vinyl butyrate and vinyl benzoate.

(9) Styrenes such as styrene, methylstyrene and chloromethylstyrene.

(10) Vinyl ketones such as methyl vinyl ketone, ethyl vinyl ketone, propyl vinyl ketone and phenyl vinyl ketone.

(11) Olefins such as ethylene, propylene, isobutylene, butadiene and isoprene.

(12) N-vinyl pyrrolidone, N-vinyl carbazole, 4-vinyl pyridine, acrylonitrile and methacrylonitrile.

(13) Unsaturated sulfonamides of (meth)acrylamides such as N-(o-aminosulfonylphenyl) (meth)acrylamide, N-(m-aminosulfonylphenyl) (meth)acrylamide, N-(p-aminosulfonylphenyl) (meth)acrylamide, N-(1-(3-aminosulfonyl)naphthyl) (meth)acrylamide and N-(2-aminosulfonylphenyl) (meth)acrylamide; and unsaturated sulfonamides of (meth)acrylic acid esters such as o-aminosulfonylphenyl (meth)acrylate, m-aminosulfonylphenyl (meth)acrylate, p-aminosulfonylphenyl (meth)acrylate and 1-(3-aminosulfonylphenyl)naphthyl (meth)acrylate.

Further, the foregoing monomers may likewise be copolymerized with other monomers copolymerizable therewith and the copolymers of the monomers listed above can be modified with, for instance, glycidyl (meth)acrylate. However, the copolymers usable in the invention are not limited to these specific examples.

The foregoing copolymers preferably comprises moieties derived from the unsaturated carboxylic acids (3) listed above and the acid value thereof preferably ranges from 0 to 10 meq/g, more preferably 0.2 to 5.0

meq/g.

Moreover, preferred molecular weight of these copolymers ranges from 10,000 to 100,000.

The foregoing copolymers, if desired, may be used, in the light-sensitive composition, in combination with polyvinyl butyral resin, polyurethane resin, polyamide resin and/or epoxy resin.

5 These alkali-soluble polymers may be used alone or in combination and the amount thereof is not more than 80% by weight on the basis of the total weight of the light-sensitive composition.

Further these alkali-soluble polymers may preferably be used in combination with a condensate of a phenol having an alkyl group carrying 3 to 8 carbon atoms as a substituent with formaldehyde such as t-butylphenol-formaldehyde resin or octylphenol-formaldehyde resin for the improvement of the ink receptivity of the resulting images.

10 The light-sensitive composition used in the invention preferably comprises, for the improvement of sensitivity, cyclic acid anhydrides, phenols and/or organic acids.

Examples of such cyclic acid anhydrides are phthalic anhydride, tetrahydrophthalic anhydride, hexahydrophthalic anhydride, 3,6-endoxy- $\Delta^4$ -tetrahydrophthalic anhydride, tetrachlorophthalic anhydride, maleic anhydride, chloromaleic anhydride,  $\alpha$ -phenylmaleic anhydride, succinic anhydride and pyromellitic anhydride.

Examples of such phenols include, for instance, bisphenol A, p-nitrophenol, p-ethoxyphenol, 2,3,4-trihydroxybenzophenone, 4-hydroxy-benzophenone, 2,4,4'-trihydroxybenzophenone, 4,4',4''-trihydroxytriphenylmethane and 4,4',3'',4'''-tetrahydroxy-3,5,3',5'-tetramethyltriphenylmethane.

20 Examples of such organic acids are, for instance, sulfonic acids, sulfinic acids, alkylsulfuric acids, phosphonic acids, phosphinic acid, phosphoric acid esters and carboxylic acids as disclosed in J.P. KOKAI Nos. Sho 60-88942 and Hei 2-96755 and specific examples thereof are p-toluenesulfonic acid, dodecylbenzenesulfonic acid, p-toluenesulfinic acid, ethylsulfuric acid, phenylphosphonic acid, phenylphosphinic acid, diphenyl phosphate, benzoic acid, isophthalic acid, adipic acid, p-toluylic acid, 3,4-dimethoxybenzoic acid, phthalic acid, terephthalic acid, 1,4-cyclohexene-2,2-dicarboxylic acid, erucic acid, 25 lauric acid, n-undecanoic acid and ascorbic acid.

The content of the foregoing cyclic acid anhydrides, phenols and/or organic acid in the light-sensitive composition preferably ranges from 0.05 to 15% by weight and more preferably 0.1 to 5% by weight on the basis of the total weight of the composition.

30 The light-sensitive composition used in the invention may further comprise, for extending the development latitude, non-ionic surfactants as disclosed in J.P. KOKAI No. Sho 62-251740 and/or amphoteric surfactants as disclosed in J.P. KOKAI No. Sho 59-121044 and Hei 4-13149.

Specific examples of non-ionic surfactants are sorbitan tristearate, sorbitan monopalmitate, sorbitan trioleate, stearyl monoglyceride, polyoxyethylene sorbitan monooleate and polyoxyethylene nonylphenyl ether.

35 Specific examples of amphoteric surfactants are alkyl di(aminoethyl)glycine, alkyl polyaminoethyl glycine hydrochloride, 2-alkyl-N-carboxyethyl-N-hydroxyethyl imidazolinium betaine and Amorgen K (trade name of an N-tetradecyl-N,N-betaine type surfactant, available from Dai-ichi Kogyo Seiyaku Co., Ltd.) and Rebon 15 (trade name of an alkyl imidazoline type one available from Sanyo Chemical Industries, Ltd.).

40 The content of the foregoing non-ionic and/or amphoteric surfactants in the light-sensitive composition preferably ranges from 0.05 to 15% by weight and more preferably 0.1 to 5% by weight on the basis of the total weight of the composition.

The light-sensitive composition used in the invention may comprise a printing out agent for obtaining a visible image immediately after exposure to light and/or a dye or pigment for coloring images.

45 A representative example of the printing out agent is a combination of a compound capable of releasing an acid through exposure to light (photolytically acid-releasing agent) with a salt-forming organic dye, for instance, a combination of o-naphthoquinonediazide-4-sulfonic acid halide with a salt-forming organic dye as disclosed in J.P. KOKAI Nos. Sho 50-36209 and Sho 53-8128; and a combination of a trihalomethyl compound with a salt-forming organic dye as disclosed in J.P. KOKAI Nos. Sho 53-36223, Sho 54-74728, 50 Sho 60-3626, Sho 61-143748, Sho 61-151644 and Sho 63-58440. Such trihalomethyl compounds include oxadiazole and triazine type compounds and both of these are excellent in stability with time and can provide clear printed out images.

Other dyes may also be used instead of or together with the foregoing salt-forming organic dyes as the agents for coloring images. Preferred dyes inclusive of the salt-forming organic dyes are, for instance, oil-soluble and basic dyes. Specific examples thereof are Oil Yellow #101 and #103, Oil Pink #312, Oil Green BG, Oil Blue BOS and #603, Oil Black BY, BS and T-505 (they are all available from Orient Chemical Industries, Co., Ltd.), Victoria Pure Blue, Crystal Violet (CI 42555), Methyl Violet (CI 42535), Ethyl Violet, Rhodamine B (CI 145170B), Malachite Green (CI 42000) and Methylene Blue (CI 52015). Particularly

preferred are those disclosed in J.P. KOKAI No. Sho 62-293247.

The light-sensitive composition used in the invention is dissolved in a solvent in which the foregoing components are soluble and then applied onto the aluminum substrate treated by the method of the invention. Examples of solvents used herein are organic solvents as disclosed in J.P. KOKAI No. Sho 62-251739 (= U.S. Patent No. 4,764,450) which may be used alone or in combination.

The light-sensitive composition is dissolved and dispersed in the solvent in a concentration ranging from 2 to 50% by weight (solid content), applied to the substrate and then dried to give a light-sensitive material.

The coated amount of the light-sensitive composition layer (light-sensitive layer) applied onto the substrate varies depending on the applications of the resulting plate, but preferably ranges from 0.3 to 4.0 g/m<sup>2</sup> (weighed after drying). As the coated amount decreases, the quantity of light required for imagewise exposure is reduced, but the strength of the film is lowered. On the other hand, as it is increased, the quantity of light required for imagewise exposure is increased, but the strength of the light-sensitive film is increased and if the product is used as a PS plate, it can provide a lithographic printing plate capable of providing a large number of acceptable copies (i.e., high printing durability).

The light-sensitive composition may comprise a surfactant such as a fluorine atom-containing surfactant as disclosed in J.P. KOKAI No. Sho 62-170950 for improving the coating properties thereof. The amount thereof to be added preferably ranges from 0.001 to 1.0% by weight, more preferably 0.005 to 0.5% by weight on the basis of the total weight of the composition.

Light-sensitive layers for negative-working PS plates usable in the invention are, for instance, those prepared from light-sensitive compositions comprising light-sensitive diazo compounds, photopolymerizable light-sensitive compositions and photocrosslinkable light-sensitive compositions. Among these, photohardenable light-sensitive copying materials comprising light-sensitive diazo compounds will be detailed below by way of example.

The light-sensitive diazo compounds used herein are, for instance, diazo resins obtained through condensation of aromatic diazonium salts with reactive carbonyl group-containing organic condensation agents, in particular, aldehydes such as formaldehyde and acetaldehyde or acetals in acidic mediums, with a condensate of p-diazodiphenylamine with formaldehyde being most typical example thereof. Methods for synthesizing these diazo resins are detailed in, for instance, U.S. Patent Nos. 2,678,498; 3,050,502; 3,311,605 and 3,277,074.

Preferably used light-sensitive diazo compounds further include, for instance, co-condensed diazo compounds of aromatic diazonium salts with substituted aromatic compounds free of diazonium groups as disclosed in J.P. KOKOKU No. Sho 49-48001, with co-condensed diazo compounds of aromatic diazonium salts with aromatic compounds substituted with alkali-soluble groups such as carboxyl and/or hydroxyl groups being particularly preferred.

Preferably used examples thereof further include light-sensitive diazo compounds obtained through condensation of alkali-soluble group-containing reactive carbonyl compounds with aromatic diazonium salts as disclosed in J.P. KOKAI Nos. Hei 4-18559, Hei 4-190361 and Hei 4-172353.

There have been known, for instance, diazo resins in which the counter anions of the diazonium salts are those derived from inorganic anions such as mineral acids, e.g., hydrochloric acid, hydrobromic acid, sulfuric acid and phosphoric acid or complex salts thereof with zinc chloride. However, particularly preferred are diazo resins which are substantially insoluble in water and soluble in organic solvents. Such preferred diazo resins are detailed in J.P. KOKOKU No. Sho 47-1167 and U.S. Patent No. 3,300,309.

Moreover, preferred diazo resins further include, for instance, those having counter anions derived from halogenated Lewis acids such as tetrafluoroboric acid, hexafluorophosphoric acid and perhalogenic acids such as perchloric acid and periodic acid as disclosed in J.P. KOKAI Nos. Sho 54-98613 and Sho 56-121031.

In addition, preferred are also include diazo resins having counter anions derived from sulfonic acid carrying long chain alkyl groups as disclosed in J.P. KOKAI Nos. Sho 58-209733, Sho 62-175731 and Sho 63-262643 (= U.S. Patent No. 3,790,556).

The amount of the light-sensitive diazo compounds usually ranges from 5 to 50% by weight and preferably 8 to 20% by weight on the basis of the total weight of the light-sensitive layer.

The light-sensitive diazo compounds used in the invention are preferably used in combination with alkaline water-soluble or swellable lipophilic polymeric materials as binders. Examples of such lipophilic polymeric compounds are the same copolymers listed above in connection with the positive-working light-sensitive compositions and having repeating units derived from the monomers (1) to (13) and molecular weights generally ranging from 10,000 to 200,000 as well as those having repeating units derived from the following monomers (14) and (15):

(14) unsaturated imides such as maleimide, N-acryloyl(meth)acrylamide, N-acetyl (meth)acrylamide, N-propionyl(meth) acrylamide and N-(p-chlorobenzoyl) (meth)acrylamide; and

(15) unsaturated monomers having, on the side chains, cross-linkable groups such as N-[2-(acryloyloxy)ethyl]-2,3-dimethylmaleimide, N-[6-(methacryloyloxy)hexyl]-2,3-dimethylmaleimide and vinyl cinnamate.

Further, other monomers copolymerizable with the foregoing monomers may be copolymerized. Moreover, the binders also include copolymers obtained by copolymerization of the foregoing monomers which are further modified with glycidyl (meth)acrylate. However, the present invention is not restricted to these specific binders.

The foregoing copolymers preferably comprises moieties derived from the unsaturated carboxylic acids (3) listed above and the acid value thereof preferably ranges from 0.2 to 10 meq/g, more preferably 0.2 to 5.0 meq/g.

Moreover, preferred molecular weight of these copolymers ranges from 10,000 to 100,000.

These copolymers, if desired, may be used, in the light-sensitive composition, in combination with polyvinyl butyral resin, polyurethane resin, polyamide resin and/or epoxy resin. Other preferred binders are novolak type resins, phenol-modified xylene resins, polyhydroxystyrene, halogenated polyhydroxystyrene and alkali-soluble resins having phenolic hydroxyl groups as disclosed in J.P. KOKAI No. Sho 51-43711.

These alkali-soluble polymers may be used alone or in combination and the amount thereof ranges from 40 to 95% by weight based on the total weight of the solid content of the light-sensitive composition.

The light-sensitive composition may comprise a sensitizing agent for improving the ink receptivity of images, such as a half ester of a styrene-maleic anhydride copolymer with an alcohol, a novolak resin or a 50% aliphatic ester of p-hydroxystyrene as disclosed in J.P. KOKAI No. Sho 55-527 (= U.S. Patent No. 4,294,905).

The light-sensitive composition used in the invention may optionally comprise a plasticizer for improving the flexibility and wear resistance of the coated light-sensitive layer. Specific examples thereof are butyl phthalyl, polyethylene glycol, tributyl citrate, diethyl phthalate, dibutyl phthalate, dihexyl phthalate, dioctyl phthalate, tricresyl phosphate, tributyl phosphate, trioctyl phosphate, tetrahydrofurfuryl oleate and oligomers and polymers of (meth)acrylic acid, with tricresyl phosphate being particularly preferred.

The light-sensitive composition used in the invention may comprise, for the improvement of stability with time, additives such as phosphoric acid, phosphonic acid, citric acid, oxalic acid, dipicolinic acid, benzenesulfonic acid, naphthalenesulfonic acid, sulfosalicylic acid, 4-methoxy-2-hydroxybenzo-phenone-5-sulfonic acid and tartaric acid.

The light-sensitive composition used in the invention may comprise a dyestuff as a printing out agent for obtaining a visible image immediately after imagewise exposure to light and/or as an agent for coloring images such as a dye or pigment.

The dyestuffs are preferably those which change color tone through the reaction with free radicals or acids. Specific examples thereof which are initially colored and converted into colorless ones, or which cause color change are triphenylmethane, diphenylmethane, oxazine, xanthene, iminonaphthoquinone, azomethine or anthraquinone type dyes such as Victoria Pure Blue (available from Hodogaya Chemical Co., Ltd.), Oil Yellow #101 and #103, Oil Pink #312, Oil Red, Oil Green BG, Oil Blue BOS and #603, Oil Black BY, BS and T-505 (they are all available from Orient Chemical Industries, Co., Ltd.), Patent Pure Blue (available from Sumitomo Mikuni Chemical Co., Ltd.), Crystal Violet (CI 42555), Methyl Violet (CI 42535), Ethyl Violet, Rhodamine B (CI 145170B), Malachite Green (CI 42000), Methylene Blue (CI 52015), Brilliant Blue, Methyl Green, Erythrosine B, Basic Fuchsin, m-Cresol Purple, Auramine, 4-p-diethylaminophenyl iminonaphthoquinone and cyano-p-diethylaminophenyl acetanilide.

On the other hand, examples of dyestuffs which are initially colorless and converted into colored ones are leuco dyes and primary and secondary arylamine type dyes such as triphenylamine, diphenylamine, o-chloroaniline, 1,2,3-triphenylguanidine, naphthylamine, diaminodiphenylmethane, p,p'-bis-dimethylaminodiphenylamine, 1,2-dianilinoethylene, p,p',p''-tris-dimethylaminotriphenylmethane, p,p'-bis-dimethylaminodiphenylmethanimine, p,p',p''-triamino-o-methyltriphenylmethane, p,p'-bis-dimethylaminodiphenyl-4-anilinonaphthylmethane and p,p',p''-triaminotriphenylmethane.

Particularly preferred dyestuffs are triphenylmethane and diphenylmethane type ones, with triphenylmethane type dyestuffs being more preferred and Victoria Pure Blue BOH being particularly preferred.

The foregoing dyestuffs are in general used in the light-sensitive composition in an amount ranging from about 0.5 to 10% by weight and preferably about 1 to 5% by weight on the basis of the total weight of the composition.

The light-sensitive compositions may further comprise cyclic acid anhydrides, phenols, organic acids and/or higher alcohols for the improvement of developability thereof. These additives are the same as those listed above in connection with the positive-working light-sensitive composition and used in the same

amount defined above.

The light-sensitive composition used in the invention is dissolved in a solvent in which the foregoing components are soluble and then applied onto the aluminum substrate treated above according to the method of the present invention. Examples of solvents used herein are organic solvents as disclosed in J.P. KOKAI No. Sho 62-251739 (= U.S. Patent No. 4,764,450) which may be used alone or in combination.

The light-sensitive composition is dissolved and dispersed in the solvent in a concentration ranging from 2 to 50% by weight (solid content), applied to the aluminum substrate and then dried to give a negative-working light-sensitive material.

The coated amount of the light-sensitive composition layer, (light-sensitive layer) applied onto the substrate varies depending on the applications of the resulting plate, but preferably ranges from 0.3 to 4.0 g/m<sup>2</sup> (weighed after drying). As the coated amount decreases, the quantity of light required for imagewise exposure is reduced, but the strength of the film is lowered. On the other hand, as it is increased, the quantity of light required for imagewise exposure is increased, but the strength of the light-sensitive film is increased and if the product is used as a PS plate, it can provide a lithographic printing plate capable of providing a large number of acceptable copies (i.e., high printing durability).

The light-sensitive composition may comprise a surfactant for improving the coating properties thereof like the positive-working light-sensitive composition discussed above.

When a PS plate is prepared, the back coat layer to be applied onto the back face of a substrate may be formed prior to the formation of the light-sensitive layer on the surface thereof, or vice versa, or they can simultaneously be applied to the substrate.

#### Mat Layer

A mat layer is applied onto the surface of the light-sensitive layer thus formed on the substrate to reduce the time required for evacuation during contact exposure using a vacuum printing frame and to prevent the formation of an indistinct image during printing. Examples of such mat layers are disclosed in J.P. KOKAI No. Sho 50-125805 and J.P. KOKOKU Nos. Sho 57-6582 and Sho 61-28986 (= U.S. Patent No. 4,268,611; 4,288,526 and 4,626,484). Alternatively, the mat layer can also be formed by fusing solid powder onto the surface of the light-sensitive layer through application of heat as disclosed in J.P. KOKOKU No. Sho 62-62337 (= U.S. Patent No. 5,028,512).

The average diameter of projections formed on the mat layer is preferably not more than 100  $\mu$ m. This is because if it exceeds the upper limit, the contact area between the light-sensitive layer and the back coat layer excessively increases when the PS plates are stored while putting them in stack increases, the slipping properties thereof is thus reduced and accordingly, scratch marks are easily formed on both surfaces of the light-sensitive and mat layers. In addition, the average height of the projections is preferably not more than 10  $\mu$ m and more preferably 2 to 8  $\mu$ m. If the average height thereof exceeds the upper limit, the formation of fineline images becomes difficult, the dot density in highlight portions decreases and the tone reproduction is also impaired. On the other hand, if it is less than 2  $\mu$ m, the resulting PS plate is insufficient in the adhesion, under vacuum, to an original film and suffers from a problem of the formation of an indistinct image during printing. The amount of the coated mat layer preferably ranges from 5 to 200 mg/m<sup>2</sup> and more preferably 20 to 150 mg/m<sup>2</sup>. If the amount thereof exceeds the upper limit, scratch marks are easily formed on the surfaces of the light-sensitive layer and the mat layer since the contact area between the light-sensitive layer and the back coat layer increases upon putting them in stack, while if it is less than the lower limit, the resulting PS plate is insufficient in the adhesion, under vacuum, to an original transparency during printing.

#### Plate-Making

The PS plate thus prepared is imagewise exposed, through an original transparency, to actinic light from a light source such as a carbon arc lamp, a mercury lamp, a metal halide lamp, a xenon lamp or a tungsten lamp and then developed.

Alkali aqueous solutions commonly known can be used as developers and replenishers for these PS plates. Examples of the alkaline agents used in the developer and replenisher compositions include inorganic alkaline agents such as sodium silicate, potassium silicate, sodium tertiary phosphate, potassium tertiary phosphate, ammonium tertiary phosphate, sodium secondary phosphate, potassium secondary phosphate, ammonium secondary phosphate, sodium carbonate, potassium carbonate, ammonium carbonate, sodium bicarbonate, potassium bicarbonate, ammonium bicarbonate, sodium borate, potassium borate, ammonium borate, sodium hydroxide, ammonium hydroxide, potassium hydroxide and lithium

hydroxide; and organic alkaline agents such as monomethylamine, dimethylamine, trimethylamine, monoethylamine, diethylamine, triethylamine, monoisopropylamine, diisopropylamine, triisopropylamine, n-butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine and pyridine.

5 In the invention, these alkaline agents may be employed alone or in combination.

Among these alkaline aqueous solutions, those preferred as developers for, in particular, positive-working PS plates are aqueous solutions of silicates such as sodium silicate and potassium silicate. This is because the developing ability of the developer can be controlled by adjusting the ratio of the silicon oxide  $\text{SiO}_2$  to the alkali metal oxide  $\text{M}_2\text{O}$  which are components of the silicate (in general expressed in terms of the molar ratio:  $[\text{SiO}_2]/[\text{M}_2\text{O}]$ ) and the concentration of the silicate. Examples of such developers are 10 aqueous solutions of sodium silicate having a molar ratio  $\text{SiO}_2/\text{Na}_2\text{O}$  ranging from 1.0 to 1.5 (i.e.,  $[\text{SiO}_2]/[\text{Na}_2\text{O}]$  ranging from 1.0 to 1.5) and an  $\text{SiO}_2$  content of 1 to 4% by weight as disclosed in J.P. KOKAI No. Sho 54-62004 (= U.S. Patent No. 4,259,434); and aqueous alkali metal silicate solutions having a ratio:  $[\text{SiO}_2]/[\text{M}]$  of 0.5 to 0.75 (i.e.,  $[\text{SiO}_2]/[\text{M}_2\text{O}]$  of 1.0 to 1.5) and an  $\text{SiO}_2$  content of 1 to 4% by weight and 15 containing at least 20% of potassium on the basis of the total gram atoms of the alkali metals present in the developer as disclosed in J.P. KOKOKU No. Sho 57-7427 (= U.S. Patent No. 4,259,434).

When the PS plates are developed with an automatic developing machine, it has been known that a large amount of PS plates can be processed over a long time without exchanging the developer in a developing tank if an aqueous solution (replenisher) having an alkalinity higher than that of the developer is 20 added to the developer. It is also preferred to adopt this replenishment in the present invention. For instance, there can preferably be used a method which comprises using an aqueous solution of sodium silicate having a molar ratio:  $\text{SiO}_2/\text{Na}_2\text{O}$  ranging from 1.0 to 1.5 (i.e.,  $[\text{SiO}_2]/[\text{Na}_2\text{O}]$  ranging from 1.0 to 1.5) and an  $\text{SiO}_2$  content of 1 to 4% by weight as disclosed in J.P. KOKAI No. Sho 54-62004 (= U.S. Patent No. 4,259,434) as a developer and continuously or intermittently adding an aqueous solution of sodium silicate 25 (replenisher) having a molar ratio:  $\text{SiO}_2/\text{Na}_2\text{O}$  ranging from 0.5 to 1.5 (or  $[\text{SiO}_2]/[\text{Na}_2\text{O}]$  ranging from 0.5 to 1.5) in proportion to the amount of the positive-working PS plates processed; and a method which makes use of an aqueous alkali metal silicate solution having a ratio:  $[\text{SiO}_2]/[\text{M}]$  of 0.5 to 0.75 (i.e.,  $[\text{SiO}_2]/[\text{M}_2\text{O}]$  of 1.0 to 1.5) and an  $\text{SiO}_2$  content of 1 to 4% by weight as a developer and an aqueous alkali metal silicate solution having a ratio:  $[\text{SiO}_2]/[\text{M}]$  of 0.25 to 0.75 (i.e.,  $[\text{SiO}_2]/[\text{M}_2\text{O}]$  of 0.5 to 1.5) as a replenisher, both 30 developer and replenisher containing at least 20% of potassium on the basis of the total gram atoms of the alkali metals present in the developer or replenisher, as disclosed in J.P. KOKOKU No. Sho 57-7427 (= U.S. Patent No. 4,259,434).

If an alkali metal silicate solution is used as such a replenisher, the activity of the replenisher increases and the amount thereof to be supplemented can be saved by reducing the molar ratio:  $[\text{SiO}_2]/[\text{M}_2\text{O}]$  of the 35 alkali metal silicate. Therefore, the alkali metal silicate solution is preferably used as a developer and this results in a reduction of the running cost and the amount of waste liquor. However, it has been known that the increase in the activity of the developer leads to dissolution of aluminum from the substrate of the PS plate and that insolubles are correspondingly formed in the developer. As such a developer system having a high activity, there can preferably be used, for instance, a combination of a developer having a high 40 activity and comprising an aqueous solution of an alkali metal silicate which has a molar ratio:  $\text{SiO}_2/\text{M}_2\text{O}$  of 0.7 to 1.5 and an  $\text{SiO}_2$  content of 1.0 to 4.0% by weight and a replenisher comprising an aqueous solution of an alkali metal silicate which has a molar ratio:  $\text{SiO}_2/\text{M}_2\text{O}$  of 0.3 to 1.0 and an  $\text{SiO}_2$  content of 0.5 to 4.0% by weight.

The developer and replenisher used in the invention for the development of the positive-working and 45 negative-working PS plates may optionally comprise various kinds of surfactants and/or organic solvents for promoting or suppressing development, for dispersing insoluble substances formed during development and for improving the ink receptivity of the image portions of the resulting lithographic printing plate. Surfactants preferably used herein are anionic, cationic, nonionic and amphoteric ones.

Examples of surfactants preferably used are nonionic surfactants such as polyoxyethylene alkyl ethers, 50 polyoxyethylene alkylphenyl ethers, polyoxyethylene polystyrylphenyl ethers, polyoxyethylene polyoxypropylene alkyl ethers, glycerin fatty acid partial esters, sorbitan fatty acid partial esters, pentaerythritol fatty acid partial esters, propylene glycol fatty acid monoesters, sucrose fatty acid partial esters, polyoxyethylene sorbitan fatty acid partial esters, polyoxyethylene sorbitol fatty acid partial esters, polyethylene glycol fatty acid esters, polyglycerin fatty acid partial esters, polyoxyethylene-modified castor oils, polyoxyethylene glycerin fatty acid partial esters, fatty acid diethanolamides, N,N-bis-2-hydroxyalkylamines, 55 polyoxyethylene alkylamines, triethanolamine fatty acid esters and trialkylamine oxides; anionic surfactants such as fatty acid salts, abietic acid salts, hydroxyalkanesulfonic acid salts, alkanesulfonic acid salts, salts of dialkylsulfosuccinic acid esters, linear alkylbenzenesulfonic acid salts, branched alkylbenzenesulfonic acid

salts, alkylnaphthalenesulfonic acid salts, alkylphenoxy polyoxyethylene propylsulfonic acid salts, polyoxyethylene alkylsulfophenyl ether salts, sodium salt of N-methyl-N-oleyltaurine, disodium salts of N-alkylsulfosuccinic acid monoamides, petroleum sulfonic acid salts, sulfated tallow oil, sulfuric acid ester salts of fatty acid alkyl esters, alkylsulfuric acid ester salts, polyoxyethylene alkyl ether sulfuric acid ester salts, fatty acid monoglyceride sulfuric acid ester salts, polyoxyethylene alkylphenyl ether sulfuric acid ester salts, polyoxyethylene styrylphenyl ether sulfuric acid ester salts, alkyl phosphoric acid ester salts, polyoxyethylene alkyl ether phosphoric acid ester salts, polyoxyethylene alkylphenyl ether phosphoric acid ester salts, partially saponified products of styrene/maleic anhydride copolymers, partially saponified products of olefin/maleic anhydride copolymers and naphthalenesulfonic acid salts/formalin condensates; cationic surfactants such as alkylamine salts, quaternary ammonium salts, polyoxyethylene alkylamine salts and polyethylene polyamine derivatives; amphoteric surfactants such as carboxy betaines, aminocarboxylic acids, sulfobetaines, aminosulfuric acid esters and imidazolines. The "polyoxyethylene" moiety of the foregoing surfactants can be replaced with polyoxyalkylene moieties such as polyoxymethylene, polyoxypropylene and polyoxybutylene and these surfactants can also be used in the present invention.

Examples of other surfactants preferably used are fluorine atom-containing ones having, in the molecules, perfluoroalkyl groups. Specific examples thereof include anionic type ones such as perfluoroalkylcarboxylic acid salts, perfluoroalkylsulfonic acid salts and perfluoroalkylphosphoric acid esters; amphoteric type ones such as perfluoroalkyl betaines; cationic type ones such as perfluoroalkyl trimethylammonium salts; and nonionic type ones such as perfluoroalkylamine oxides, perfluoroalkyl ethylene oxide adducts, oligomers carrying perfluoroalkyl groups and hydrophilic groups, oligomers carrying perfluoroalkyl groups and lipophilic groups, oligomers carrying perfluoroalkyl groups, hydrophilic groups and lipophilic groups and urethanes carrying perfluoroalkyl groups and lipophilic groups.

The foregoing surfactants may be used alone or in combination and the amount thereof added to the developer preferably ranges from 0.001 to 10% by weight and more preferably 0.01 to 5% by weight.

The organic solvents which may be added to the developer are preferably selected from those having solubility in water of not more than about 10% by weight, in particular not more than 5% by weight. Examples of the organic solvent include 1-phenylethanol, 2-phenylethanol, 3-phenyl-1-propanol, 4-phenyl-1-butanol, 4-phenyl-2-butanol, 2-phenyl-1-butanol, 2-phenoxyethanol, 2-benzyloxyethanol, o-methoxybenzyl alcohol, m-methoxybenzyl alcohol, p-methoxybenzyl alcohol, benzyl alcohol, cyclohexanol, 2-methylcyclohexanol, 3-methylcyclohexanol, 4-methylcyclohexanol, N-phenyl ethanolamine and N-phenyl diethanolamine. The amount of the organic solvents preferably ranges from 0.1 to 5% by weight with respect to the total weight of the developer practically employed. The amount of the organic solvent is closely related to that of the surfactant. More specifically, the amount of the surfactant should be increased with the increase in that of the organic solvent. This is because if the amount of the anionic surfactant is low and that of the organic solvent is great, the organic solvent is not completely solubilized in water and as a result, good developing properties of the composition cannot be ensured.

The developer and replenisher used in the invention for developing the PS plates may further comprise reducing agent for preventing the contamination of the resulting lithographic printing plate and this is particularly effective in the development of negative-working PS plates comprising light-sensitive diazonium salts. Examples of reducing agents preferably used are organic reducing agents, for instance, phenolic compounds such as thiosalicic acid, hydroquinone, menthol, methoxyquinone, resorcin and 2-methylresorcin; amine compounds such as phenylenediamine and phenyl hydrazine; and inorganic reducing agents such as sodium, potassium and ammonium salts of inorganic acids such as sulfinic acid, hydrosulfurous acid, phosphorous acid, hydrogenphosphorous acid, dihydrogenphosphorous acid, thiosulfuric acid and dithionous acid. Among these, those having particularly excellent effect of preventing contamination are sulfites. These reducing agents are preferably used in an amount ranging from 0.05 to 5% by weight on the basis of the weight of the developer practically employed.

The developer and replenisher may also comprise organic carboxylic acids. Preferred are aliphatic and aromatic carboxylic acids having 6 to 20 carbon atoms. Specific examples of the aliphatic carboxylic acids are caproic acid, enanthic acid, caprylic acid, lauric acid, myristic acid, palmitic acid and stearic acid with the alkanic acids having 8 to 12 carbon atoms being particularly preferred. These aliphatic acids may be unsaturated ones having, in the carbon chain, double bonds or those having branched carbon chains.

Examples of the aromatic carboxylic acids are compounds having carboxyl groups on the aromatic rings such as benzene, naphthalene and anthracene rings, for instance, o-chlorobenzoic acid, p-chlorobenzoic acid, o-hydroxybenzoic acid, p-hydroxybenzoic acid, o-aminobenzoic acid, p-aminobenzoic acid, 2,4-dihydroxybenzoic acid, 2,5-dihydroxybenzoic acid, 2,6-dihydroxybenzoic acid, 2,3-dihydroxybenzoic acid, 3,5-dihydroxybenzoic acid, gallic acid, 1-hydroxy-2-naphthoic acid, 3-hydroxy-2-naphthoic acid, 2-hydroxy-1-naphthoic acid, 1-naphthoic acid and 2-naphthoic acid, with the hydroxynaphthoic acids being particularly

effective.

The foregoing aliphatic and aromatic carboxylic acids are preferably used in the form of sodium, potassium or ammonium salt for improving the solubility thereof in water. The amount of the organic carboxylic acids used in the developer is not restricted to a particular range. However, if they are used in an amount of less than 0.1% by weight, the desired effect thereof is not anticipated, while if they are used in an amount of more than 10% by weight, any further effect thereof is not anticipated and if other additives are simultaneously used, they interrupt the dissolution thereof. Therefore, the amount of the carboxylic acids preferably ranges from 0.1 to 10% by weight and more preferably 0.5 to 4% by weight on the basis of the total weight of the developer practically used.

The developer and replenisher used in the invention may optionally comprise conventionally known compounds such as antifoaming agents, water softeners and/or organic boron-containing compounds as disclosed in J.P. KOKOKU No. Hei 1-57895 (= U.S. Patent No. 4,500,625).

Examples of water softeners include polyphosphoric acids and sodium, potassium and ammonium salts thereof; polyaminocarboxylic acids such as ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, triethylenetetraminehexaacetic acid, hydroxyethylethylenediaminetriacetic acid, nitrilotriacetic acid, 1,2-diaminocyclohexanetetraacetic acid and 1,3-diamino-2-propanoltetraacetic acid; and ammonium, potassium and sodium salts thereof; aminotri(methylenephosphonic acid), ethylenediaminetetra(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), triethylenetetraminehexa(methylenephosphonic acid), hydroxyethylethylenediaminetri(methylenephosphonic acid) and 1-hydroxyethane-1,1-diphosphonic acid, and ammonium, potassium and sodium salts thereof.

The optimum amount of the water softener varies depending on the chelating ability of a specific softener, the hardness and the amount of hard water used, but the amount thereof in general ranges from 0.01 to 5% by weight and preferably 0.01 to 0.5% by weight on the basis of the total weight of the developer practically used. If the amount of the softener is less than the lower limit, the desired effect cannot be anticipated, while if it exceeds the upper limit, images are adversely affected and cause color blinding or the like.

The balance of the developer and replenisher used in the invention is water, but they may optionally comprise other various additives currently known in the art.

It is preferred to prepare the developer and replenisher in the form of stock solutions having contents of the components higher than those practically used and diluted prior to use from the viewpoint of transportation. In this case, the degree of concentration is preferably selected such that each component does not cause separation and precipitation.

The PS plate thus developed is then subjected to post-treatments with, for instance, washing water, a rinsing solution containing, for instance, a surfactant and/or a desensitization solution containing, for instance, gum arabic or a starch derivative. Any combination of these treatments can be used as the post-treatment for the PS plate thus prepared.

Recently, there have been used automatic developing machines for PS plates for the purpose of rationalization and standardization of the plate-making operations in the fields of plate making or printing industries. The automatic developing machine of this type generally comprises a developing zone and a post-treatment zone and more specifically it comprises a device for conveying PS plates to be processed, baths filled with various processing solutions and spray devices, wherein an imagewise exposed PS plate is developed by spraying each processing solution, sent up by a pump, thereon through a spray nozzle while the PS plate is horizontally conveyed. Alternatively, there has recently been known a method in which an imagewise exposed PS plate is developed by conveying the plate while it is dipped in a bath filled with a processing solution through the action of dipped guide rolls. In such an automatic processing, the PS plate can be processed while supplementing replenishers to the corresponding processing baths in proportion to the amount of the processed PS plates and the operation time.

The lithographic printing plate prepared from a PS plate which makes use of the aluminum substrate brush-grained by the method of the present invention hardly causes, on a printing press, background contamination and narrowing and/or collapse of the shadowed portion thereof even when only a small amount of dampening water is used. Therefore, the printing plate can easily be handled even by an inexperienced person and can stably provide high quality copies as compared with conventional lithographic printing plates.

The method of the present invention will further be explained in more detail with reference to the following non-limitative working Examples and the effects practically attained by the present invention will also be discussed in detail in comparison with Comparative Examples given below.

All "%" are by weight, unless otherwise indicated.

## Example 1

An aluminum plate of JIS A 1050 having a thickness of 0.24 mm was subjected to a brush-graining treatment using two kinds of rotary nylon brushes detailed below while supplying, to the surface of the plate, a suspension comprising particles of pumice stone having an average particle size of about 21  $\mu\text{m}$  dispersed in water. The first brush had a bristle length of 100 mm, a bristle diameter of 0.95 mm and a bristle-implantation density of 70 bristles/cm<sup>2</sup>, while the second brush had a bristle length of 80 mm, a bristle diameter of 0.295 mm and a bristle-implantation density of 670 bristles/cm<sup>2</sup>. The diameter of the first and second brushes (including the bristles) was 40 cm. These two brushes were both rotated at 250 rpm. After sufficiently washing with water subsequent to the brush-graining, the plate was etched by immersing in a 10% sodium hydroxide solution at 60°C for 25 seconds, followed by washing with running water, neutralization and washing with a 20% nitric acid solution and water-washing. The aluminum plate was then electrolytically surface-roughened in a 1% aqueous nitric acid solution at an anodic voltage,  $V_A$ , of 12.7 V such that the quantity of electricity at the anode time was 160 coulomb/dm<sup>2</sup> using a sinusoidal alternating waved current. At this stage, the surface roughness thereof was determined to be 0.79  $\mu\text{m}$  (expressed in terms of the Ra unit). Thereafter, it was desmutted by immersing in a 1% aqueous sodium hydroxide solution at 40°C for 30 seconds and then in a 30% sulfuric acid aqueous solution at 60°C for 40 seconds and anodized in a 20% aqueous solution of sulfuric acid at a current density of 2 A/dm<sup>2</sup> so that the thickness of the resulting anodized layer was 1.6 g/m<sup>2</sup> to give an aluminum substrate.

An underlying coating solution having the following composition was applied onto the surface of the substrate thus treated and dried at 80°C for 30 seconds.

The coated amount of the underlying coating solution (weighed after drying) was found to be 30 mg/m<sup>2</sup>.

Underlying Coating Solution	
Component	Amount (g)
aminoethylphosphonic acid	0.10
phenylphosphonic acid	0.15
$\beta$ -alanine	0.10
methanol	40
pure water	60

Thus, a substrate was prepared.

Then a light-sensitive solution having the following composition was applied onto the substrate and dried at 110°C for one minute to give a positive-working PS plate. The coated amount of the solution (weighed after drying) was found to be 1.7 g/m<sup>2</sup>.

Light-Sensitive Solution

	Component	Amount (g)
5	ester of 1,2-diazonaphthoquinone-5-sulfonyl chloride	0.45
	with pyrogallol/acetone resin (product disclosed	
	in Example 1 of U.S. Patent No. 3,635,709)	
10	cresol/formaldehyde novolak resin (m-/p- ratio: 6:4;	1.1
	weight-average molecular weight 3,000; number-	
15	average molecular weight 1,100; unreacted cresol	
	content 0.7%)	
20	m-cresol/formaldehyde novolak resin (weight-average	0.3
	molecular weight 1,700; number-average molecular	
	weight 600; unreacted cresol content 1%)	
25	poly[N-(p-aminosulfonylphenyl)acrylamide-co-n-butyl	0.2
	acrylate-co-diethylene glycol monomethyl ether	
30	methacrylate] (molar ratio of monomers = 40/40/20;	

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weight-average molecular weight 40,000; number-average molecular weight 20,000)

5	p-(n-octyl)phenol/formaldehyde resin (the product disclosed in U.S. Patent No. 4,123,279)	0.02
10	naphthoquinone-1,2-diazide-4-sulfonic acid chloride	0.01
	tetrahydrophthalic anhydride	0.1
	benzoic acid	0.02
15	4-[p-N,N-bis(ethoxycarbonylmethyl)aminophenyl]-2,6-bis(trichloromethyl)-s-triazine	0.01
20	4-[p-N-(p-hydroxybenzoyl)aminophenyl]-2,6-bis(trichloromethyl)-s-triazine	0.02
	2-trichloromethyl-5-(4-hydroxystyryl)-1,3,4-oxadiazole	0.01
25	dye. Victoria Pure Blue BOH whose counter anion is exchanged to 1-naphthalenesulfonate anion	0.02
30	Modiper F-200 (a fluorine atom-containing surfactant available from Nippon Oil and Fats Co., Ltd., a 30% by weight solution in a mixed solvent: methyl ethyl ketone/methyl isobutyl ketone)	0.06
35	Megafac F-177 (a fluorine atom-containing surfactant available from Dainippon Ink and Chemicals, Inc.; a 20% by weight solution in methyl isobutyl ketone)	0.02
40	methyl ethyl ketone	15
45	1-methoxy-2-propanol	10

50 A mat layer was formed on the light-sensitive layer thus applied by electrostatically spraying an aqueous solution of methyl methacrylate/ethyl acrylate/sodium acrylate (68/20/12) copolymer according to the method disclosed in Example 1 of J.P. KOKOKU No. Sho 61-28986.

The PS plate thus formed was imagewise exposed, in a vacuum printing frame, to light from a 3 KW metal halide lamp at a distance of 1 m through a positive transparency for 50 seconds and then processed in an automatic developing machine STABLON 900D (available from Fuji Photo Film Co., Ltd.) which was supplied with a 5.26% aqueous solution (pH 12.7) of sodium silicate having a molar ratio SiO<sub>2</sub>/Na<sub>2</sub>O of 1.74 as a developer and FR-3 (diluted 8 times with water; available from Fuji Photo Film Co., Ltd.) as a rinsing solution. The resulting lithographic printing plate was allowed to stand over one day and fitted to a printing

press to evaluate the quality thereof.

In the printing operation, there were used KOR-D available from Hidelberg Co., Ltd. as a printing press, EU-3 (diluted 101 times with water; available from Fuji Photo Film Co., Ltd.) as dampening water and Mark Five New Sumi Ink available from Toyo Ink Mfg. Co., Ltd. as a printing ink.

5 The dampening water was decreased on the printing press and the lithographic printing plate was observed with naked eyes to determine the degree of contamination of the non-image area with the ink which was evaluated according to the following criteria: A ●●● completely free of contamination; B ●●● almost no contamination; C ●●● slightly contaminated; and D ●●● contaminated.

10 The narrowing of the distance between half tone dots in a shadowed portion was judged by determining whether 2% of the half tone dots in the portion were opened or not when the dampening water was decreased and evaluated according to the following criteria: A ●●● completely opened; B ●●● approximately opened; C ●●● slightly narrowed; and D ●●● collapsed.

15 In this respect, preferred acceptable copies can be obtained upon using a lithographic printing plate whose contamination of non-image area and narrowing of shadowed portions are both not less than the evaluation criterion B.

20 As a result, it was found that the lithographic printing plate, which made use of the substrate prepared by the method of the present invention, hardly caused background contamination and narrowing or collapse of the shadowed portion thereof even when only a small amount of dampening water was used. The lithographic printing plate could provide acceptable copies of more than 100,000. The results thus obtained are summarized in the following Table 1.

#### Examples 2 to 6

25 The same procedures used in Example 1 were repeated except that an aluminum plate was subjected to brush graining while using combinations of first brushes selected from three kinds of those having thick bristles (bristle diameters of 0.95 mm, 0.72 mm and 0.57 mm) with second brushes selected from two kinds of those having fine bristles (bristle diameters of 0.295 mm and 0.21 mm) detailed in Table 1. The diameter of the brushes including the bristles was 40 cm. Each of the first brushes had a bristle length of 100 mm and implantation densities of 70, 120 and 200 bristles/cm<sup>2</sup>, respectively while each of the second brushes 30 had a bristle length of 80 mm and implantation densities of 670 and 1000 bristles/cm<sup>2</sup>, respectively. The results obtained in these Examples are listed in Table 1.

#### Comparative Examples 1 to 5

35 The same procedures used in Example 1 were repeated except that the brush graining treatment was performed using brushes provided with bristles having the same diameter. The combinations of brushes and the results thus obtained are summarized in Table 1.

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Table 1

Combination of Brushes						Surface Rough- ness Ra ( $\mu$ m)	Backgro- und Con- taminat- tion	Narrow ing of Shad. Port. <sup>1)</sup>
First Brush		Second Brush						
Bristle Length (mm)								
0.95	0.72	0.57	0.295	0.21				
Example								
1	*			*	0.79	B	A	
2	*			*	0.78	B	A	
3		*		*	0.74	B	A	
4		*		*	0.71	B	A	
5			*	*	0.69	A	A	
6			*	*	0.63	A	A	
Comp. Ex.								
1	*				0.82	D	A	
2		*			0.76	C	A	
3			*		0.70	C	A	
4				*	0.43	A	C	
5				*	0.35	A	D	

\*: This indicates that each corresponding brush was used.

1): Narrowing of shadowed portions.

In Table 1, the surface roughness Ra was determined using a surface roughness-determining device (surface profilometer) SURFCOM 300B (available from Tokyo Seimitsu Co., Ltd.; tracer 10  $\mu$ mR).

Examples 7 to 9 and Comparative Examples 6 and 7

The same procedures used in Example 1 were repeated except that at least two first or second brushes were used to perform brush graining. The combinations of brushes and the results thus obtained are summarized in Table 2.

Table 2

Combination and No. of Brushes	Surface	Backgro-	Narrow			
<u>First Brush</u>	<u>Second Brush</u>	Rough-	und Con- ing in			
<u>Bristle Length (mm)</u>		ness	taminat- Shad.			
<u>0.72</u>	<u>0.57</u>	<u>0.295</u>	<u>Ra (<math>\mu</math>m)</u>	<u>tion</u>	<u>Port.</u>	
Example						
5	--	1	1	0.69	A	A
7	--	2	1	0.70	A	A
8	--	5	1	0.71	A	A
9	1	1	1	0.73	A	A
Comp. Ex.						
6	--	2	--	0.72	C	A
7	--	--	2	0.37	A	C

The results shown in Tables 1 and 2 clearly indicate that the lithographic printing plates of Examples 1 to 9 which made use of the substrates prepared by the method of the present invention respectively exhibited excellent quality since they hardly caused background contamination and narrowing or collapse of the shadowed portions as compared with those prepared in Comparative Examples 1 to 7.

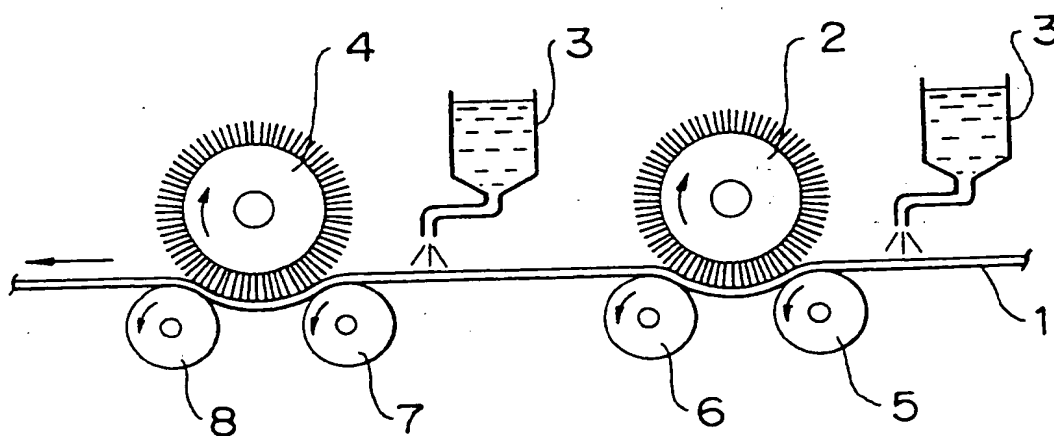
#### Claims

1. A method of preparing an aluminum substrate for lithographic printing plate comprising a brush-graining step which comprises surface-roughening an aluminum plate with at least two kinds of brushes whose bristles have different diameters.
2. The method of claim 1 wherein the brushes each comprises a roll-like base and nylon bristles implanted in the base; or comprises a base having small holes and bundles of nylon bristles implanted in the holes of the base; or a channel roll type brush.
3. The method of claim 2 wherein the brush comprises nylon bristles having a bristle length ranging from 10 to 200 mm as determined after implantation.
4. The method of claim 2 wherein the brush has a density of implanted bristles ranging from 50 to 300 bristles/cm<sup>2</sup>.
5. The method of claim 1 wherein the two kinds of brushes are the first brush whose bristles have a diameter of not less than 0.57 mm and not more than 1.20 mm and the second brush whose bristles have a diameter of not less than 0.10 mm and not more than 0.34 mm; and the brush used in the final

brush-graining process is the second brush.

- 5 6. The method of claim 5 wherein the two kinds of brushes are the first brush whose bristles have a diameter of not less than 0.64 mm and not more than 1.00 mm and the second brush whose bristles have a diameter of not less than 0.20 mm and not more than 0.30 mm; and the brush used in the final brush-graining process is the second brush.
- 10 7. The method of claim 5 wherein the number of the first brushes used ranges from 1 to 10 and the number of the second brushes used ranges from 1 to 3.
8. The method of claim 1 wherein the brush-graining process is carried out using a slurry which comprises an abrasive having an average particle size of from 15 to 35  $\mu$  dispersed in water in a concentration ranging from 10 to 70% by weight.
- 15 9. The method of claim 1 wherein brush-graining process is carried out till the center line average height (Ra) of the aluminum plate falls within the range of from 0.5 to 1.0  $\mu$ .
- 20 10. The method of claim 1 wherein it further comprises, after the brush-graining process, an electrolytically surface-roughening process and an anodization process.

FIG. 1





European Patent  
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# EUROPEAN SEARCH REPORT

Application Number  
EP 93 11 6973

## DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.5)
X	US-A-2 637 929 (W.J.HAUSMAN) * claims; figure *	1-10	B41N3/04
Y	EP-A-0 213 371 (FUJI PHOTO FILM CO., LTD.,) * example 1 *	1-10	
X	US-A-2 707 359 (S.V.WORTHEN et Al.) * claims *	1,2	
Y	EP-A-0 118 740 (HOECHST A.G.) * page 6, line 29 - page 7, line 21; claims 1,5 * * page 13, line 19 - line 24 * * page 29, line 25 - page 30, line 1 *	1-10	
A	PATENT ABSTRACTS OF JAPAN vol. 011, no. 213 (M-605)10 July 1987 & JP-A-62 028 293 (FUJI PHOTO FILM CO., LTD.,) 6 February 1987 * abstract *	8	
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 055 (M-669)1 February 1988 & JP-A-62 202 795 (FUJI PHOTO FILM CO., LTD.,) 7 September 1987 * abstract *	8	TECHNICAL FIELDS SEARCHED (Int.Cl.5) B41N

TECHNICAL FIELDS  
SEARCHED (Int.Cl.5)

The present search report has been drawn up for all claims

Place of search

THE HAGUE

Date of completion of the search

21 December 1993

Examiner

Rasschaert, A

### CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone  
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